

CLAIMS

1. A catalyst system capable of catalysing the carbonylation of an ethylenically unsaturated compound, which system is obtainable by combining:
 - a) a metal of Group VIB or Group VIIIB or a compound thereof,
 - b) a bidentate phosphine, arsine, or stibine ligand, and
 - 10 c) an acid,

wherein said ligand is present in at least a 2:1 molar excess compared to said metal or said metal in said metal compound, and that said acid is present in at least a 2:1 molar excess compared to said ligand.
2. A catalyst system as claimed in claim 1 wherein the ratio of said ligand to said metal is in the range 5:1 to 750:1.
- 20 3. A catalyst system as claimed in claim 1 wherein the ratio of said ligand to said metal is in the range 10:1 to 500:1.
- 25 4. A catalyst system as claimed in claim 1 wherein the ratio of said ligand to said metal is in the range 20:1 to 40:1.
- 30 5. A catalyst system as claimed in any of the preceding claims wherein the ratio of said acid to said ligand is in the range 5:1 to 95:1.

6. A catalyst system as claimed in any of the preceding claims wherein the ratio of said acid to said ligand is in the range 20:1 to 40:1.

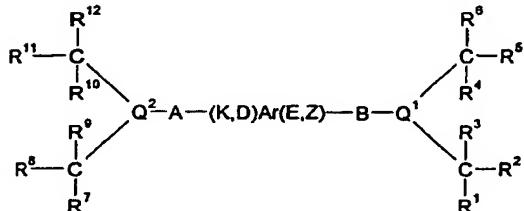
5 7. A catalyst system as claimed in any of the preceding claims wherein the molar ratio of said acid to said metal is in the range 10:1 to 75000:1.

10 8. A catalyst system as claimed in any of the preceding claims wherein the molar ratio of said acid to said metal is in the range 100:1 to 25000:1.

15 9. A catalyst system as claimed in any of the preceding claims wherein the molar ratio of said acid to said metal is in the range 200:1 to 400:1.

10. A catalyst system as claimed in any preceding claim wherein said ligand is a bidentate phosphine ligand.

20 11. A catalyst system as claimed in any preceding claim wherein said ligand is of general formula (I)



(I)

wherein:

25 Ar is a bridging group comprising an optionally substituted aryl moiety to which the phosphorus atoms are linked on available adjacent carbon atoms;

A and B each independently represent lower alkylene;

5 K, D, E and Z are substituents of the aryl moiety (Ar) and each independently represent hydrogen, lower alkyl, aryl, Het, halo, cyano, nitro, OR¹⁹, OC(O)R²⁰, C(O)R²¹, C(O)OR²², NR²³R²⁴, C(O)NR²⁵R²⁶, C(S)R²⁵R²⁶, SR²⁷, C(O)SR²⁷, or -J-Q³(CR¹³(R¹⁴)(R¹⁵)CR¹⁶(R¹⁷)(R¹⁸) where J represents lower alkylene; or two adjacent groups selected from K, Z, D and E together with the carbon atoms of the aryl ring to which they are attached form a further phenyl ring, which is optionally substituted by one or more substituents selected from hydrogen, lower alkyl, halo, cyano, nitro, OR¹⁹, OC(O)R²⁰, C(O)R²¹, C(O)OR²², NR²³R²⁴, C(O)NR²⁵R²⁶, C(S)R²⁵R²⁶, SR²⁷ or 10 C(O)SR²⁷;

15 R¹³ to R¹⁸ each independently represent lower alkyl, aryl, or Het;

20 R¹⁹ to R²⁷ each independently represent hydrogen, lower alkyl, aryl or Het;

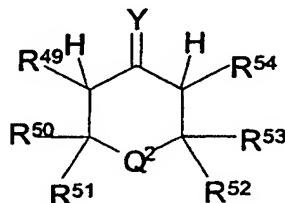
25 R¹ to R¹² each independently represent lower alkyl, aryl, or Het;

30 Q¹, Q² and Q³ (when present) each independently represent phosphorous, arsenic or antimony and in the latter two cases references to phosphine or phosphorous above are amended accordingly, with preferably both Q¹ and Q² representing phosphorus, more preferably all of Q¹, Q² and Q³ (when present) representing phosphorus.

12. A catalyst system as claimed in claim 11 wherein at least one $(CR^xR^yR^z)$ group attached to Q^1 and/or Q^2 , i.e. $CR^1R^2R^3$, $CR^4R^5R^6$, $CR^7R^8R^9$, $CR^{10}R^{11}R^{12}$, $CR^{13}R^{14}R^{15}$, or $CR^{16}R^{17}R^{18}$, may instead be represented by the group (Ad) 5 wherein:

Ad each independently represent an optionally substituted adamantyl or congressyl radical bonded to the phosphorous atom via any one of its tertiary carbon atoms, the said optional substitution being by one or more substituents selected from hydrogen, lower alkyl, halo, cyano, nitro, OR^{19} , $OC(O)R^{20}$, $C(O)R^{21}$, $C(O)OR^{22}$, $NR^{23}R^{24}$, $C(O)NR^{25}R^{26}$, $C(S)R^{25}R^{26}$, SR^{27} or $C(O)SR^{27}$; or if both $(CR^xR^yR^z)$ groups attached to either or both Q^1 and/or Q^2 , or Q^3 (if present) together with either Q^1 or Q^2 (or Q^3) as appropriate, form an optionally substituted 2-phosphatricyclo[3.3.1.1{3,7}]decyl group or derivative 10 thereof, or form a ring system of formula 15

20



wherein

25 R^{49} , and R^{54} , each independently represent hydrogen, lower alkyl or aryl;

R^{50} to R^{53} , when present, each independently represent hydrogen, lower alkyl, aryl or Het; and

Y represents oxygen, sulfur or N-R⁵⁵; and R⁵⁵, when present, represents hydrogen, lower alkyl or aryl.

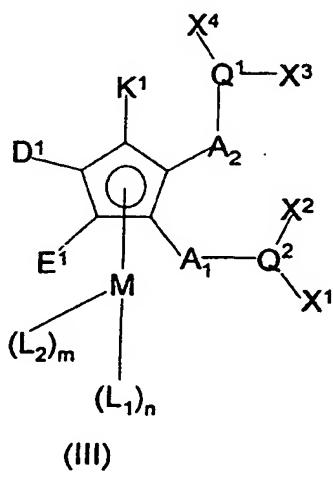
13. A catalyst system as claimed in either of claims 11
5 and 12 wherein said ligand is represented as:



10 wherein Ar, A, B, K, D, E and Z, Q¹, Q², and Q³, and R¹ to R²⁷ are as defined in claim 11 except that K, D, E and Z may represent -J-Q³(Ad)_w(CR¹³(R¹⁴)(R¹⁵)_x instead of -J-Q³(CR¹³(R¹⁴)(R¹⁵))CR¹⁶(R¹⁷)(R¹⁸) and Ad is as defined in claim 12,

15 S & U = 0, 1 or 2 provided that S + U ≥ 1;
T & V = 0, 1 or 2 provided that T + V ≤ 3;
W & X = 0, 1 or 2.

14. A catalyst system as claimed in any of claims 1 to 10
20 wherein said ligand is of general formula (III).



wherein:

A_1 and A_2 , and A_3 , A_4 and A_5 (when present), each independently represent lower alkylene;

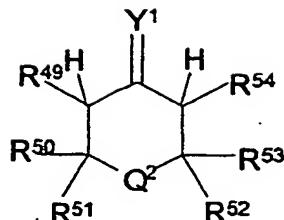
5 K^1 is selected from the group consisting of hydrogen, lower alkyl, aryl, Het, halo, cyano, nitro, $-OR^{19}$, $-OC(O)R^{20}$, $-C(O)R^{21}$, $-C(O)OR^{22}$, $-N(R^{23})R^{24}$, $-C(O)N(R^{25})R^{26}$, $-C(S)(R^{27})R^{28}$, $-SR^{29}$, $-C(O)SR^{30}$, $-CF_3$ or $-A_3-Q^3(X^5)X^6$;

10 D^1 is selected from the group consisting of hydrogen, lower alkyl, aryl, Het, halo, cyano, nitro, $-OR^{19}$, $-OC(O)R^{20}$, $-C(O)R^{21}$, $-C(O)OR^{22}$, $-N(R^{23})R^{24}$, $-C(O)N(R^{25})R^{26}$, $-C(S)(R^{27})R^{28}$, $-SR^{29}$, $-C(O)SR^{30}$, $-CF_3$ or $-A_4-Q^4(X^7)X^8$;

15 E^1 is selected from the group consisting of hydrogen, lower alkyl, aryl, Het, halo, cyano, nitro, $-OR^{19}$, $-OC(O)R^{20}$, $-C(O)R^{21}$, $-C(O)OR^{22}$, $-N(R^{23})R^{24}$, $-C(O)N(R^{25})R^{26}$, $-C(S)(R^{27})R^{28}$, $-SR^{29}$, $-C(O)SR^{30}$, $-CF_3$ or $-A_5-Q^5(X^9)X^{10}$;

20 or both D^1 and E^1 together with the carbon atoms of the cyclopentadienyl ring to which they are attached form an optionally substituted phenyl ring:

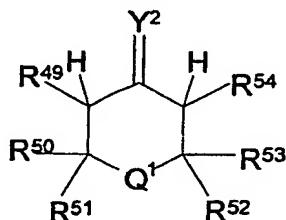
25 X^1 represents $CR^1(R^2)(R^3)$, congressyl or adamantyl, X^2 represents $CR^4(R^5)(R^6)$, congressyl or adamantyl, or X^1 and X^2 together with Q^2 to which they are attached form an optionally substituted 2-phosphatricyclo[3.3.1.1{3,7}]decyl group or derivative thereof, or X^1 and X^2 together with Q^2 to which they are attached form a ring system of formula IIIa



(IIIa)

X³ represents CR⁷(R⁸)(R⁹), congressyl or adamantyl, X⁴ represents CR¹⁰(R¹¹)(R¹²), congressyl or adamantyl, or X³ and X⁴ together with Q¹ to which they are attached form an optionally substituted 2-phospha-5

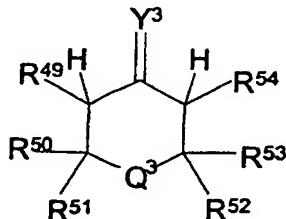
tricyclo[3.3.1.1{3,7}]decyl group or derivative thereof, or X³ and X⁴ together with Q¹ to which they are attached form a ring system of formula IIIb



(IIIb)

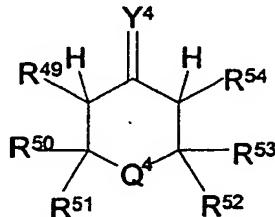
X⁵ represents CR¹³(R¹⁴)(R¹⁵), congressyl or adamantyl, X⁶ represents CR¹⁶(R¹⁷)(R¹⁸), congressyl or adamantyl, or X⁵ and X⁶ together with Q³ to which they are attached form an optionally substituted 2-phospha-5

tricyclo[3.3.1.1{3,7}]decyl group or derivative thereof, or X⁵ and X⁶ together with Q³ to which they are attached form a ring system of formula IIIc



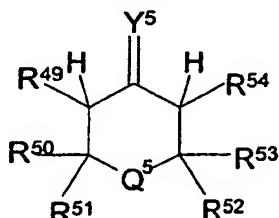
(IIIc)

5 X^7 represents $CR^{31}(R^{32})(R^{33})$, congressyl or adamantyl, X^8 represents $CR^{34}(R^{35})(R^{36})$, congressyl or adamantyl, or X^7 and X^8 together with Q^4 to which they are attached form an optionally substituted 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group or derivative thereof, or X^7 and X^8 together with Q^4 to which they are attached form a ring system of formula IIId



(III d)

10 X^9 represents $CR^{37}(R^{38})(R^{39})$, congressyl or adamantyl, X^{10} represents $CR^{40}(R^{41})(R^{42})$, congressyl or adamantyl, or X^9 and X^{10} together with Q^5 to which they are attached form an optionally substituted 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group or derivative thereof, or X^9 and X^{10} together with Q^5 to which they are attached form a ring system of formula IIIe



(III e)

20 Q^1 and Q^2 , and Q^3 , Q^4 and Q^5 (when present), each independently represent phosphorus, arsenic or antimony;

M represents a Group VIB or VIIIB metal or metal cation thereof;

L₁ represents an optionally substituted cyclopentadienyl, indenyl or aryl group;

5 L₂ represents one or more ligands each of which are independently selected from hydrogen, lower alkyl, alkylaryl, halo, CO, P(R⁴³)(R⁴⁴)R⁴⁵ or N(R⁴⁶)(R⁴⁷)R⁴⁸;

10 R¹ to R¹⁸ and R³¹ to R⁴², when present, each independently represent hydrogen, lower alkyl, aryl, halo or Het;

15 R¹⁹ to R³⁰ and R⁴³ to R⁴⁸, when present, each independently represent hydrogen, lower alkyl, aryl or Het;

R⁴⁹, R⁵⁴ and R⁵⁵, when present, each independently represent hydrogen, lower alkyl or aryl;

20 R⁵⁰ to R⁵³, when present, each independently represent hydrogen, lower alkyl, aryl or Het;

25 Y¹, Y², Y³, Y⁴ and Y⁵, when present, each independently represent oxygen, sulfur or N-R⁵⁵;

n = 0 or 1;

and m = 0 to 5;

30 provided that when n = 1 then m equals 0, and when n equals 0 then m does not equal 0.

15. A catalyst system as claimed in claim 14 wherein if both K^1 represents $-A_3-Q^3(X^5)X^6$ and E^1 represents $-A_5-Q^5(X^9)X^{10}$, then D^1 represents $-A_4-Q^4(X^7)X^8$.
- 5 16. A catalyst system as claimed in any of claims 12 to 15, wherein adamantyl represents unsubstituted adamantyl or adamantyl substituted with one or more unsubstituted C_1-C_8 alkyl substituents, or a combination thereof.
- 10 17. A catalyst system as claimed in any of claims 12 to 16, wherein 2-phospha-adamantyl represents unsubstituted 2-phospha-adamantyl or 2-phospha-adamantyl substituted with one or more unsubstituted C_1-C_8 alkyl substituents, or a combination thereof.
- 15 18. A catalyst system as claimed in any of claims 12 to 17, wherein 2-phospha-adamantyl includes one or more oxygen atoms in the 2-phospha-adamantyl skeleton.
- 20 19. A catalyst system as claimed in any of claims 12 to 18, wherein congressyl represents unsubstituted congressyl.
- 25 20. A catalyst system according to any preceding claim wherein the metal or compound thereof is palladium.
21. A catalyst system according to claim 20 wherein the palladium is in the metal form.
- 30 22. A catalyst system according to any preceding claim, wherein the catalyst system includes in a liquid reaction medium a polymeric dispersant dissolved in a

liquid carrier, said polymeric dispersant being capable of stabilising a colloidal suspension of particles of the Group VI or VIIIB metal or metal compound of the catalyst system within the liquid carrier.

- 5 23. A process for the carbonylation of an ethylenically unsaturated compound comprising contacting an ethylenically unsaturated compound with carbon monoxide and a hydroxyl group containing compound in the presence of a catalyst system as claimed in any preceding claim.
- 10 24. A process according to claim 23, wherein the carbonylation of an ethylenically unsaturated compound is performed in one or more aprotic solvents.
- 15 25. A process according to either of claims 23 and 24, wherein suitable ethylenically unsaturated compounds include ethene, propene, hexene, vinyl compounds such as vinyl acetates, heptene, octene, nonene, decene, undecene, dodecene, etc up to C₃₀, i.e. having from 2 to 30 carbon atoms, which may be linear or branched, cyclic or uncyclic or part cyclic and in which the double bond may take any suitable position in the carbon chain and which includes all stereoisomers thereof.
- 20 26. A reaction medium comprising one or more reactants, and a catalyst system comprising, or obtainable by combining, at least a Group VIB or VIIIB metal or metal compound, a bidentate phosphine, arsine, or stibine ligand, and an acid, wherein said ligand is
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present in at least a 2:1 molar excess compared to said metal or said metal in said metal compound, and that said acid is present in at least a 2:1 molar excess compared to said ligand.

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27. A reaction medium comprising one or more reactants, and a catalyst system as claimed in any one of claims 1 to 22.

10 28. A reaction medium as claimed in either of claims 26 and 27 wherein the amount of free acid present in the medium is greater than 500ppm.

15 29. Use of a system comprising, or obtainable by combining:

- a) a metal of Group VIB or Group VIIIB or a compound thereof,
- b) a bidentate phosphine, arsine, or stibine ligand, preferably a bidentate phosphine ligand, and
- c) an acid,

25 wherein said ligand is present in at least a 2:1 molar excess compared to said metal or said metal in said metal compound, and that said acid is present in at least a 2:1 molar excess compared to said ligand, as a catalyst in the carbonylation of an ethylenically unsaturated compound.

30 30. A catalyst system substantially as described herein with reference to the examples and figures.

31. A process substantially as described herein with reference to the examples and figures.
32. A reaction medium substantially as described herein with reference to the examples and figures.
33. Use substantially as described herein with reference to the examples and figures.
34. A catalyst system capable of catalysing the carbonylation of an ethylenically unsaturated compound, said system comprising:
 - a) a metal of Group VIB or Group VIIIB or a compound thereof,
 - b) a bidentate phosphine, arsine, or stibine ligand, preferably a bidentate phosphine ligand, and
 - c) an acid,
- wherein said ligand is present in at least a 2:1 molar excess compared to said metal or said metal in said metal compound, and that said acid is present in at least a 2:1 molar excess compared to said ligand.
35. A process for the carbonylation of an ethylenically unsaturated compound comprising contacting an ethylenically unsaturated compound with carbon monoxide and a hydroxyl group containing compound in the presence of a catalyst system, said system comprising:
 - a) a metal of Group VIB or Group VIIIB or a compound thereof,

- b) a bidentate phosphine, arsine, or stibine ligand, preferably a bidentate phosphine ligand, and
- c) an acid,

5 wherein said ligand is present in at least a 2:1 molar excess compared to said metal or said metal in said metal compound, and that said acid is present in at least a 2:1 molar excess compared to said ligand.

10 36. A complex capable of catalysing the carbonylation of an ethylenically unsaturated compound, said complex obtainable by combining:

- a) a metal of Group VIB or Group VIIIB or a compound thereof,
- b) a bidentate phosphine, arsine, or stibine ligand, preferably a bidentate phosphine ligand, and
- c) an acid,

20 wherein said ligand is present in at least a 2:1 molar excess compared to said metal or said metal in said metal compound, and that said acid is present in at least a 2:1 molar excess compared to said ligand.

25 37. A process for the carbonylation of an ethylenically unsaturated compound with carbon monoxide and a hydroxyl group containing compound in the presence of a complex, said complex as defined in claim 36.